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THERMAL DECOMPOSITION OF BASIC LEAD CARBONATES: A COMPARISON OF HYDROCERUSSITE AND PLUMBONACRITE *

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ABSTRACT

The decomposition of synthetic hydrocerussite, $Pb_3(OH)_2(CO_3)_2$, and plumbonacrite, $Pb_{10}O(OH)_6(CO_3)_6$, in both CO_2 and inert atmospheres, was compared using differential thermal analysis and thermogravimetry. The overall weight losses, upon decomposition to PbO, were in good agreement with calculated values. The initial dehydration steps for hydrocerussite and plumbonacrite yielded 2 $PbCO_3 \cdot PbO$, and a mixture of 2 $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot PbO$, respectively, consistent with the lower carbonate content of plumbonacrite than hydrocerussite. These differences do not account for discrepancies among the numerous previous reports on hydrocerussite decomposition. Rather, the decomposition route of a lead carbonate seems to be highly sensitive to the nature of its formation.

INTRODUCTION

The thermal decomposition of hydrocerussite, $Pb_3(OH)_2(CO_3)_2$, has been widely studied [1–7], but there is disagreement about the sequence of intermediate products of the type $x\ PbCO_3 \cdot y\ PbO$. Pannetier et al. [2], Komoda et al. [3], Andreeva and Limar [4], Sarig and Kahana [5], and Ball and Casson [6] all reported 2 $PbCO_3 \cdot PbO$ as the initial product of dehydration, in accordance with reaction (1)

$$Pb_3(OH)_2(CO_3)_2 \rightarrow 2\ PbCO_3 \cdot PbO + H_2O \qquad (1)$$

However, Yamaguchi et al. [7] only saw this phase at elevated pressures of CO_2, and they pointed out that the X-ray diffraction (XRD) data reported by Pannetier et al. [2] for 2 $PbCO_3 \cdot PbO$ actually correspond to those for a mixture of cerussite ($PbCO_3$) and $PbCO_3 \cdot PbO$. Three groups [3–5] recorded

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a well-defined thermogravimetric plateau corresponding to completion of reaction (1). Ball and Casson [6] did not, but they did identify 2 $PbCO_3 \cdot PbO$ in partly decomposed hydrocerussite, using XRD.

The 1 : 1 compound, $PbCO_3 \cdot PbO$, was observed only by Andreeva and Limar [4], Ball and Casson [6] and Yamaguchi et al. [7]. Sarig and Kahana [5] postulated a 2 : 3 intermediate on the basis of an inflection in a thermogravimetric curve, but their data can also be interpreted in terms of the more commonly encountered 1 : 2 phase. Pannetier et al. [2], Ball and Casson [6] and Andreeva and Limar [4] all reported $PbCO_3 \cdot 2\ PbO$ as the final intermediate before formation of the oxide. Yamaguchi et al. [7] again saw it only at elevated pressures of CO_2, whereas Komoda et al. [3] saw it as a minor intermediate in the decomposition of 2 $PbCO_3 \cdot PbO$ in vacuo. Grisafe and White [8] determined the stability fields of $PbCO_3$, PbO and the 2 : 1, 4 : 3, 1 : 1 and 1 : 2 $PbCO_3 : PbO$ phases at CO_2 pressures in the range 1.5–140 MPa, and estimated the stability limits of three of the $PbCO_3 : PbO$ phases at atmospheric pressure, 0.1 MPa (the 4 : 3 phase is stable only above ~ 38 MPa).

In 1966, Olby [9] resolved earlier confusion about the crystallographic unit-cell dimensions of hydrocerussite. He demonstrated the existence of two solids, with similar stoichiometries: hydrocerussite, $Pb_3(OH)_2(CO_3)_2$, and plumbonacrite, $Pb_{10}O(OH)_6(CO_3)_6$ [$= 3\ Pb_3(OH)_2(CO_3)_2 \cdot PbO$]. Taylor and Lopata [10] recently determined stability and solubility relationships between PbO, plumbonacrite, hydrocerussite and cerussite ($PbCO_3$) in aqueous systems at 22 °C. Brooker et al. [11] reported IR and Raman spectroscopic data for hydrocerussite and plumbonacrite. We thought that a comparison of the thermal behaviour of hydrocerussite and plumbonacrite might shed some light on the confusion about the decomposition of hydrocerussite, and we wished to evaluate thermal analysis as a tool for distinguishing between hydrocerussite and plumbonacrite. Our interest first arose from the possible use of these solids to immobilize ^{14}C, which is formed by various neutron reactions in nuclear fission reactors.

EXPERIMENTAL

Starting materials

Hydrocerussite was prepared by controlled hydrolysis of cerussite in either K_2CO_3 solution (0.3 mol dm^{-3}) or aqueous KOH (pH maintained at 11 by automatic titration), at room temperature (~ 22 °C). Plumbonacrite was prepared by hydrolysis of hydrocerussite in an alkaline carbonate solution (~ 0.5 mol dm^{-3}, pH ≈ 13) at 100 °C. Details of these preparations have been published elsewhere [10]. The solids were checked for purity by XRD, using a Philips PW-1150 powder diffractometer, with Cu$K\alpha$ radiation and a diffracted-beam monochromator, and referring to Olby's XRD data [9]. No impurities were detected in the hydrocerussite, whereas the plumbonacrite contained up to 5% of unconverted hydrocerussite. Both solids were microcrystalline; scanning electron microscopy (Cambridge Mk. II stereoscan) showed that each consisted of thin irregular platelets.

Thermal analysis

The decomposition of plumbonacrite and hydrocerussite was monitored by differential thermal analysis (DTA) and thermogravimetry (TG). Experiments were run in an atmosphere of CO_2, Ar (DTA only) or N_2 (TG only), at a gas flow-rate of 30 $cm^3\ min^{-1}$, and a heating rate of 2.5 (TG only) or 10 °C min^{-1}. The samples (10–20 mg) were held in platinum microcrucibles. The DTA experiments were run on a DuPont 990 thermal analyser coupled to a platinum-wire wound, vertical-tube furnace, using Pt/Pt–13%Rh thermocouples to monitor the temperature difference between the sample and the corundum (α-Al_2O_3) reference material. The TG experiments were run on a Perkin-Elmer TGS-1 thermobalance, using the Curie temperatures of magnetic standards [12] for the temperature calibration. In several TG runs, partly decomposed samples were cooled to room temperature and examined by XRD, using a 114.6-mm diameter Debye–Scherrer camera, Ni-filtered Cu$K\alpha$ radiation, and reference diffraction data from Grisafe and White [8].

RESULTS

The TG traces for decomposition of hydrocerussite and plumbonacrite in N_2 at a heating rate of 10 °C min^{-1} could not be resolved into separate stages. Hydrocerussite showed a small, progressive weight loss up to 200 °C, followed by an accelerating decomposition that was complete at 350 °C. Plumbonacrite showed little weight loss below 270 °C, but then decomposed rapidly from there to 350 °C. The total weight losses in both N_2 and CO_2 atmospheres were consistent with the overall decomposition reactions (2) and (3)

$$Pb_3(OH)_2(CO_3)_2 \rightarrow 3\ PbO + H_2O + 2\ CO_2 \qquad (2)$$

Observed weight loss (5 runs), 13.5–14.2%; average, 13.8%; theoretical, 13.67%.

$$Pb_{10}O(OH)_6(CO_3)_6 \rightarrow 10\ PbO + 3\ H_2O + 6\ CO_2 \qquad (3)$$

Observed weight loss (5 runs), 12.0–12.6%; average, 12.3%; theoretical, 12.47%.

The decomposition sequence was better resolved in TG experiments run with a CO_2 atmosphere, because the decarbonation steps were displaced to higher temperatures than the dehydration. This is consistent with the expected increase in equilibrium CO_2 partial pressure with increasing temperature for any reaction involving CO_2 evolution [8]. The resolution of the TG curves was further improved when the heating rate was reduced to 2.5 °C

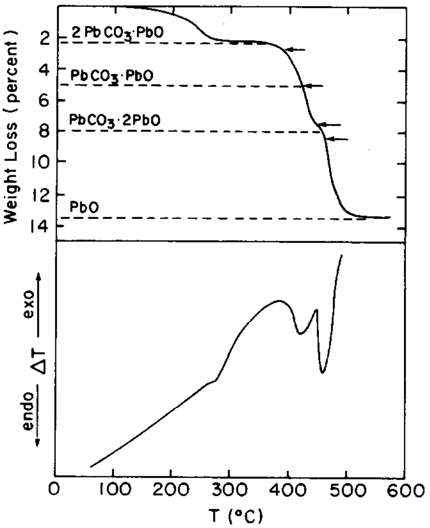

Fig. 1. TG (upper) and DTA traces obtained from hydrocerussite in a CO_2 atmosphere at heating rates of 2.5 and 10°C min^{-1}, respectively. (— — —) Theoretical weight losses; arrows show the stages of weight loss at which runs were terminated for identification of intermediate products by XRD. The DTA baseline slopes upward at an angle of about 40°.

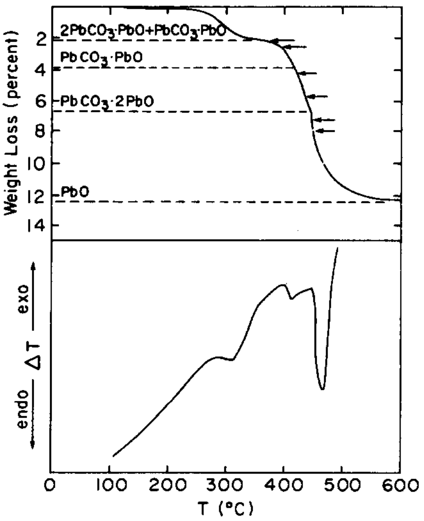

Fig. 2. TG (upper) and DTA traces obtained from plumbonacrite in a CO_2 atmosphere at heating rates of 2.5 and 10°C min^{-1}, respectively. Dashed lines and arrows have the same meanings as in Fig. 1.

min^{-1}. The DTA curves were satisfactorily resolved at 10 °C min^{-1}. These thermoanalytical curves are presented in Figs. 1 and 2. The XRD results, obtained from partly decomposed samples, are given in Table 1.

Decomposition of hydrocerussite in CO_2

The first stage of this decomposition occurred gradually between about 150 and 275 °C (Fig. 1). The weight loss was consistent with the formation of $2\ PbCO_3 \cdot PbO$, according to eqn. (1), and this was confirmed by XRD (Table 1). The TG curve shows a poorly resolved discontinuity in the subsequent decomposition, near 450 °C and at the weight loss calculated for the formation of $PbCO_3 \cdot 2\ PbO$. The XRD data showed only trace quantities of $PbCO_3 \cdot PbO$, and confirmed that the principal decomposition route followed eqns. (4) and (5)

$$2\ PbCO_3 \cdot PbO \rightarrow PbCO_3 \cdot 2\ PbO + CO_2 \qquad (4)$$

$$PbCO_3 \cdot 2\ PbO \rightarrow 3\ PbO + CO_2 \qquad (5)$$

The DTA curve (Fig. 1) shows three endothermic features, which correspond to the three stages of weight loss. These TG and DTA results thus differ in detail from all the previous reports on hydrocerussite decomposition.

Decomposition of plumbonacrite in CO_2

The initial stage of this decomposition was less drawn out than that for hydrocerussite, and occurred at higher temperatures (~ 250–340 °C). The weight loss was consistent with eqn. (6)

$$Pb_{10}O(OH)_6(CO_3)_6 \rightarrow 2[2\ PbCO_3 \cdot PbO] + 2[PbCO_3 \cdot PbO] + 3\ H_2O \qquad (6)$$

TABLE 1

Identity of solid phases in partly decomposed hydrocerussite and plumbonacrite, from TG runs in a CO_2 atmosphere

Starting material	T_{max} (°C) [a]	Wt. loss (%)	$2\ PbCO_3 \cdot PbO$	$PbCO_3 \cdot PbO$	$PbCO_3 \cdot 2\ PbO$	PbO (litharge)
Hydrocerussite	330	2.7	Major	—	—	—
	416	5.1	Major	Trace	Minor	—
	425	7.5	Minor	—	Major	—
	452	8.5	Trace	—	Major	—
Plumbonacrite	360	2.2	Major	Major	—	—
	405	2.6	Major	Major	Trace	—
	417	4.3	Major	Major	Major	—
	430	5.8	Minor	Minor	Major	—
	447	7.3	—	—	Major	Trace
	450	8.0	—	—	Major	Minor

[a] Temperature at which TG run was terminated; these temperatures may differ from those indicated by the arrows in Figs. 1 and 2, because of slight variations in the TG traces from run to run.

The XRD measurements (Table 1) confirmed that both 2 $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot PbO$ were major products of decomposition. The deficiency of carbonate in plumbonacrite precludes the formation of pure 2 $PbCO_3 \cdot PbO$ without the uptake of CO_2, as in eqn. (7)

$$3\ Pb_{10}O(OH)_6(CO_3)_6 + 2\ CO_2 \rightarrow 10[2\ PbCO_3 \cdot PbO] + 9\ H_2O \qquad (7)$$

There was no evidence of such uptake during the TG runs.

The subsequent decomposition of the oxycarbonate mixture again showed a slight discontinuity, at about 440 ° C, near the weight loss expected for the formation of $PbCO_3 \cdot 2\ PbO$. The XRD measurements showed that the relative intensities of the 2 $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot PbO$ diffraction peaks remained approximately constant, while their absolute intensities fell and $PbCO_3 \cdot 2\ PbO$ peaks appeared as the decomposition progressed. It therefore seems that $PbCO_3 \cdot 2\ PbO$ was formed concurrently, and at similar rates, by reactions (4) and (8)

$$3[PbCO_3 \cdot PbO] \rightarrow 2[PbCO_3 \cdot 2\ PbO] + CO_2 \qquad (8)$$

and it subsequently decomposed to PbO by reaction (5), as in the case of hydrocerussite.

The conclusion is supported by the DTA curve (Fig. 2), which shows only three features, and does not resolve reactions (4) and (8). The second feature is proportionately smaller than that in the DTA curve for hydrocerussite, consistent with the smaller quantity of CO_2 evolved.

DISCUSSION

We did observe distinct differences in the thermal decomposition reactions of hydrocerussite and plumbonacrite, mainly in the thermogravimetric profile and products of the initial dehydration step. However, given the inconsistencies between various reports of hydrocerussite decomposition, these differences are insufficient to distinguish between hydrocerussite and plumbonacrite. The only reliable difference between the two is in the total weight losses (see eqns. 2 and 3). Even this difference is too small for accurate analyses of mixtures, or materials containing any inert impurity. Hydrocerussite and plumbonacrite are much more readily distinguished by XRD [9] or vibrational spectroscopy [11].

The total weight losses shown for hydrocerussite decomposition, in refs. 5–7, are all close to the calculated value, so confusion with plumbonacrite seems unlikely. Pannetier et al. [13] reported a total weight loss of 12.2% for "Clichy" white lead, which they identified as $Pb(OH)_2 \cdot PbCO_3$. It is possible that this material was plumbonacrite, although the only intermediate product observed in this case was $PbCO_3 \cdot PbO$. The diffraction pattern they reported was not unlike that of plumbonacrite, bearing in mind the problem of preferred orientation with basic lead carbonates [9]. The reported IR spectrum is also similar, although not identical, to that of plumbonacrite [11].

There is clearly a delicate balance between the kinetics of nucleation and growth of 2 $PbCO_3 \cdot PbO$, $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2$ PbO during the thermal decomposition of lead carbonates (the decomposition of cerussite, $PbCO_3$, shows a variability similar to that of hydrocerussite [14]). These kinetics are expected to depend strongly on particle size, morphology and defect properties, which probably accounts for the different behaviour of hydrocerussite obtained from different sources.

Warne and Bayliss [15] have shown that the positions and relative intensities of features in the DTA curve of cerussite vary with particle size. Sarig and Kahana [5] also concluded that the degree of crystal perfection is an important factor in determining the course of thermal decomposition of lead carbonates. Komoda et al. [16], as cited by Yamaguchi et al. [14], found that the route for isothermal decomposition of cerussite depended in part on the conditions of preparation of the cerussite.

The equilibrium stability fields of the three oxycarbonates are narrow. Grisafe and White [8] estimated the following stability limits at a CO_2 partial pressure of about 0.1 MPa (i.e., atmospheric pressure): 2 $PbCO_3 \cdot PbO$, 204 ± 20 to 283 ± 15 °C; $PbCO_3 \cdot PbO$, 283 ± 15 to 373 ± 15 °C; $PbCO_3 \cdot 2$ PbO, 373 ± 15 to 435 ± 10 °C. Evidently, superheating by a few tens of degrees can permit the metastable formation of one or more phases, and/or the omission of a phase from the decomposition sequence. It is significant that the discrepancies between literature reports on the decomposition of hydrocerussite and cerussite are greatest for the lower-temperature processes involving formation of 2 $PbCO_3 \cdot PbO$ and/or $PbCO_3 \cdot PbO$, and smallest for the higher-temperature decompositions of $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2$ PbO. The latter two processes usually commence within 20° of the equilibrium temperatures estimated by Grisafe and White [8]. In their study of the CO_2-pressure dependence of cerussite decomposition, Yamaguchi et al. [14] found that only the final step, from $PbCO_3 \cdot 2$ PbO to PbO (eqn. 5), occurs close to equilibrium. The earlier stages occurred only after 20–60° of superheating. There is thus no "correct" decomposition sequence, but rather the confusion in the literature reflects the sensitivity of the decomposition route of a lead carbonate to the origin of the starting material.

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